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<b>(21) International Application Number:</b> PCT/AU93/00562 <b>(22) International Filing Date:</b> 29 October 1993 (29.10.93)  <b>(30) Priority data:</b> PL 5631 30 October 1992 (30.10.92) AU  <b>(71) Applicant (for all designated States except US):</b> COMMON-WEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION [AU/AU]; Limestone Avenue, Campbell, ACT 2601 (AU).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> STEELE, Robert, John [AU/AU]; 154 Old South Head Road, Vaucluse, NSW 2030 (AU). JIANG, Xiang, Zhou [CN/AU]; 9/104 Cambramatta Road, Mosman, NSW 2088 (AU).		<b>(74) Agent:</b> F.B. RICE & CO.; 28A Montague Street, Balmain, NSW 2041 (AU).  <b>(81) Designated States:</b> AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SULPHUR DIOXIDE FILM  <b>(57) Abstract</b>  Single and multi-layer materials and polymeric films for use in packaging of produce are disclosed. The material and polymeric films incorporate a sulphur dioxide-liberating compound(s) and one or more of the following additives: an acid compound(s); a hygroscopic compound(s); a polymer(s) which degrades to produce an acid; a compound(s) which becomes or generates an acid or acidic gas in a humid environment; wherein the amount and identity(ies) of the additive(s) may be selected to provide a predetermined, controlled rate of sulphur dioxide liberation.		

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Sulphur Dioxide Film

The present invention relates to a film which releases sulphur dioxide, and in particular to the use of such films in packaging materials.

5 Sulphites are commonly used as preservatives in food and other industries. They have been used to prevent enzymic and non-enzymic browning as well as growth of spoilage microorganisms, for over two thousand years. Despite this long history of use sulphur dioxide  
10 can cause severe respiratory disfunction in asthmatics and its reaction with components of biological systems has led to concern that its use as a preservative may be harmful to health. Toxicity of sulphur dioxide to the human respiratory system has received considerable  
15 attention since it was demonstrated that it is a major contributor to smogs. Inhalation of sulphur dioxide may severely increase resistance to pulmonary flow which in susceptible people such as asthmatics may have fatal consequences.

20 These concerns have led to sulphite being removed from the "generally recognized as safe" (GRAS) list and for organisations such as the US National Restaurant Association to ask its members to discontinue sodium bisulphite use.

25 Australia exports many foods containing sulphur dioxide, fresh grapes, dried tree fruits and wine are examples. The maximum permitted level of sulphur dioxide in dried tree fruits in Australia is 3000 mg  $\text{SO}_2 \cdot \text{kg}^{-1}$  which is higher than the levels permitted  
30 in some of the countries to which the fruit are exported. Some products containing sulphite at levels above the importing permitted levels have been confiscated.

35 Furthermore there is pressure by health authorities and legislators to further reduce the permitted levels

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of sulphite in foods.

Therefore the need exists to find ways by which the levels of sulphite in foods may be reduced or eliminated.

Packaging materials incorporating a sulphur  
5 dioxide-liberating sulphite(s) have now been proposed  
which liberate sulphur dioxide upon permeation of water  
vapour. By avoiding the direct contact of the sulphite  
compounds with the produce, these materials offer a  
higher level of safety. However, to be useful these  
10 materials must be able to generate sulphur dioxide over  
extended periods so as to compensate for the loss of  
sulphur dioxide caused by its reactivity with food  
components such as oxygen.

European Patent Specification No. 0351636 describes  
15 one example of this kind of packaging material. The  
packaging material comprises two sheets of synthetic or  
other material pervious to water vapour and sulphur  
dioxide, laminated together with a suitable substance  
such as paraffin wax. Dispersed within the laminating  
20 substance is a material which, in the presence of  
moisture, liberates sulphur dioxide. This packaging  
material does however, have a number of disadvantages  
including a rather complex manufacture and a limited  
range of applications. Further, the packaging material  
25 described does not allow for the fact that different  
types of produce consume sulphur dioxide at varying  
rates and thus, the packaging material may not be  
suitable for some types of produce.

The present inventors have now developed a  
30 packaging material which aims to provide advantages over  
the prior art or ameliorate at least one of the  
disadvantages mentioned above.

Thus, in a first aspect the present invention  
provides a polymeric film material for use in the  
35 packaging of produce incorporating a sulphur

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dioxide-liberating compound(s) and one or more of the following additives:

- an acid compound(s);
- a hygroscopic compound(s);
- 5       - a polymer(s) which degrades to produce an acid;
- a compound(s) which becomes or generates an acid or acidic gas in a humid environment;

wherein the amount and identity(ies) of the additive(s) are selected to provide a predetermined, controlled rate of sulphur dioxide liberation.

Suitable sulphur dioxide-liberating compounds for use in the present invention include those listed by the United States Food and Drug Administration under 21 CFR Ch.1 - Part 182, including sodium sulphite, sodium hydrogen sulphite, sodium metabisulphite. Other suitable sulphur dioxide-liberating compounds include calcium sulphite, calcium hydrogen sulphite, calcium metabisulphite, salts of thiosulphuric acid and organic sulphur dioxide-liberating agents. Mixtures of these materials may also be suitable. For produce sensitive to salt damage, it is preferable to use non-hygroscopic salts such as calcium sulphite.

Suitable acid compound(s) may vary depending upon the other components, but may include those acidulants typically used in food processing such as stearic acid, benzoic acid, citric acid, ascorbic acid, succinic acid, tartaric acid, sorbic acid, acetic acid, propionic acid, adipic acid, fumaric acid, lactic acid, malic acid, phosphoric acid and their salts. Mixtures comprising stearic acid can also be useful because the stearic acid acts as a coupling agent between the other acid(s) and the polymer and sulphur dioxide-liberating compound(s). The identity(ies) and quantity of the acid(s) used can be selected to achieve a predetermined rate of sulphur dioxide liberation. This may be achieved because

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moisture permeating through the film results in the generation of hydrogen ions from the acid compound(s), which in turn positively influences the liberation of sulphur dioxide from the sulphur dioxide-liberating compound(s). The amount of hydrogen ions generated is related to the amount and the dissociation constant of the acid compound(s) present in the film.

Suitable hygroscopic compounds include hygroscopic salts such as salts of acetic acid, salts of hydrochloric acid, salts of carbonic acid, polyhydric alcohols such as glycerol and propylene glycol and hygroscopic polymers. These compounds may be used to control the sulphur dioxide liberation rate because they absorb moisture which, in turn, triggers the liberation of sulphur dioxide.

Suitable polymers which degrade to produce an acid include neoprene, poly(lactic acid), poly(glycolic acid) and co-polymers, poly(anhydrides) and poly(ortho-esters).

Other materials, such as anhydrides, lactones or lactide, which become acid in a humid environment, may also be used to achieve a predetermined, controlled liberation of sulphur dioxide due to their different rates of hydrolysis and different acidities.

Suitable polymers for the production of the films include members of the polyolefin family due to their high permeability to sulphur dioxide. Low temperature processing, low density polyethylene are particularly preferred polyolefins (e.g. Compol 4202 and LDPE 4203). Other polymers with acid functional groups such as acid co-polymers EAA or EMAA may also be suitable carriers of the sulphur dioxide-liberating compound(s). These polymers have superior adhesion to aluminium foil and greater toughness when compared to LDPE. Polymers such as poly(vinyl chloride), ethylene-vinyl alcohol, cellulose acetate, ethyl cellulose or starch may also be

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used. Ionomers such as Dupont's SURLYN resins may also be used. However, the most preferred polymer is poly (vinyl alcohol) due to the high loadings of sulphur dioxide-liberating compounds that can be achieved with this polymer. Poly (vinyl alcohol) is also biodegradable and recyclable.

The polymeric film material according to the invention may be a single-layer or multi-layer film. In the case of multi-layer films, the sulphur dioxide-liberating compound(s) and one or more additive(s), may be present within each or separate layers of the film. This latter arrangement offers an advantage in that direct contact between the produce and the layer containing the sulphur dioxide-liberating compound(s) may be avoided. Further, poly (vinyl alcohol) films need to be made from aqueous solutions. The addition of the sulphur dioxide-liberating compound(s) and the additive(s) to the aqueous poly (vinyl alcohol) solution can cause an unwanted release of sulphur dioxide. This difficulty may be overcome by producing a multi-layer film wherein the film layers containing the sulphur dioxide-liberating compound(s) or additive(s) are made separately, and subsequently laminated together. A similar result may be achieved where one or more of the layers used comprises paper or other porous material.

Thus, in a second aspect the present invention provides a material for use in packaging of produce, comprising at least two laminated layers, wherein at least one layer incorporates a sulphur dioxide-liberating compound(s) and at least one other layer incorporates one or more of the following additives:

- an acid compound(s);
- a hygroscopic compound(s),

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- a polymer(s) which degrades to produce an acid;
- a compound(s) which becomes or generates an acid or acidic gas in a humid environment;

the arrangement and characteristics of the layers being  
5 such that the additive(s) cause or influence the  
liberation of sulphur dioxide.

Preferably, the packaging material according to the  
second aspect of the invention comprises at least two  
laminated polymeric film layers. More preferably, it  
10 comprises at least two laminated poly (vinyl alcohol)  
film layers. Again, the amount and identity(ies) of the  
additive(s) may be selected to provide a predetermined,  
controlled rate of sulphur dioxide liberation.

The invention further relates to a method for  
15 producing a multi-layer film or material according to  
the first or second aspect, comprising separately  
forming at least one layer incorporating the sulphur  
dioxide-liberating compound(s) and at least one layer  
incorporating the one or more additives, and thereafter  
20 laminating the film layers together.

Polymeric film materials according to either aspect  
of the invention may be used to wrap the produce prior  
to surrounding with typical packaging material such as  
corrugated cardboard to provide greater mechanical  
25 strength. Alternatively, the polymeric film materials  
may be used as a lining for typical packaging material.

As used herein the term "produce" is used in its  
broadest sense and is intended to cover all forms of  
produce including but not limited to wine, flowers,  
30 grapes, dried fruits such as apricots, peaches and  
pears, marine produce in particular prawns, cut flowers  
and the like.

The materials of the present invention are also  
useful in reducing peroxide in cases where peroxide is  
35 used to sterilise the film or where hydrogen peroxide is



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formed in oxygen scavenging applications, for example those applications using oxidation of ascorbic acid. The sulphur dioxide saps up hydrogen peroxide.

5 It may also be advantageous to include oxidant agent(s) in the film or material. Suitable oxidants include copper sulphate and iron sulphate.

10 In order that the nature of the present invention may be more clearly understood, preferred forms thereof will now be described with reference to the following non-limiting examples.

**EXAMPLE 1: FILM FABRICATION**

**Sample Preparation**

15 All films were prepared at room temperature and under ambient conditions in a fume cupboard. All contact surfaces including polymers and other additives were dry, and sulphite salts were micronised to (about 20 $\mu$  .

**Cellulose acetate films**

- 20 1. Cellulose acetate powder was mixed with glycerol and then the mixture was dissolved in acetone in a conical flask. A mechanical stirrer Janke & Kunel IKA-WERK was used continuously for at least 8 hours. The resulting solution was clear and very viscous.
- 25 2. An organic acidulant was added and dissolved into the solution.
3. An inorganic salt (calcium sulphite or sodium disulphite), which had been previously dried and ground, was suspended in the solution.
4. The film was cast onto a glass plate with the solution using a glass rod as a screed.
- 30 5. The film was dried in the fume cupboard at room temperature.

**Polyvinyl chloride (PVC) films**

- 35 1. Ethanol was added to PVC powder (Corvic) in a conical flask and mixed thoroughly. At this stage the

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polymer was wetted and may be swollen.

2. Tetrahydrofuran was added to the polymer. The mixture was stirred intensively for at least 6 hours. At this stage, the solution was clear and very viscous.

5 No particles were visually detectable inside the solution.

3. An organic acidulant was added and dissolved in the solution.

10 4. An inorganic sulphite salt, which was previously dried and ground, was suspended into the solution.

5. A film was cast onto a glass plate with the solution using a glass rod as a screed.

6. The film was dried in a fume cupboard at room temperature.

15 Polyvinyl alcohol (PVOH) films

1. PVOH was dissolved in water using a microwave oven to heat the mixture to the boiling point. The mixture was stirred with a glass rod to remove large lumps. At this stage, the solution is very viscous but not very  
20 clear and small particles are visually detectable. Continuous stirring over a water bath for at least 8 hours clarifies the solution.

2. An inorganic sulphite salt was either suspended (for calcium sulphite) or dissolved (for sodium  
25 disulphite) into the solution over the water bath.

3. A film was cast onto a PVC board with the solution using a glass rod.

4. The sulphite salt-containing film was dried at room temperature in a fume cupboard.

30 5. A film containing an organic acidulant was made in the same fashion.

6. Contact between the acidulant and the sulphite salt films was avoided until they were dry to touch.

35 7. For two-layer-films, an acidulant film and a sulphite salt film can be ironed together at temperature

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around 200°C for 2-3 seconds. A laminating machine (Bench-Top Rotary Printing and Coating Machine - RK Print Coat Instruments) may be used to make the two layers contact better.

5 8. Three-layer-films were made in an analagous manner.

Alternatively, films according to the invention may be cast using vented extruders fitted with a Blown film die (1") and film take-off tower. The take-off tower governs the rate at which the blown film is drawn from  
10 the die, thereby controlling film thickness.

#### C. Examples of films

Specific recipes for films are provided in Tables 1-4.

#### 15 Method for Determining the Liberation Rate of Sulphur Dioxide

The same procedure was used for determining the liberation rate of sulphur dioxide at both temperatures (i.e. 0°C and 15°C) tested.

Air from a cylinder is passed through Fisher  
20 Mulligan wash bottles. The first bottle is filled with water and the second is filled with potassium sulfate to provide constant relative humidity (approximately 98%). The air is then passed through two test tubes connected in series at approximately 30ml/min. The film or  
25 material to be tested is placed in the first test tube and the second test tube is filled with 3% hydrogen peroxide solution. Released sulphur dioxide will be absorbed and oxidized to sulfuric acid. The resulting acid is titrated with sodium hydroxide.

#### 30 EXAMPLE 2: MEASUREMENT OF SULPHUR DIOXIDE LIBERATION RATES FROM FILMS

Liberation rates of sulphur dioxide from various films according to the invention were tested using the method described in Example 1. Other sulphur  
35 dioxide-liberating materials (i.e. Kraft paper, UVAS

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sachet) were tested using the same method for comparison. Results are presented in Tables 5-7.

Table 5 shows that three-layer poly (vinyl alcohol) films using ascorbic acid and benzoic acid produced a low level of sulphur dioxide liberation. In contrast, the same film construction using lactone showed a vastly greater sulphur dioxide liberation over the duration of the experiment (80.7 days). Steady state release of sulphur dioxide was achieved with this film after about 21 days.

Table 6 shows that in single layer PVC films, greater levels of sulphur dioxide liberation with citric acid and a citric acid-succinic acid mixture than with succinic acid alone. Two-layer poly (vinyl alcohol) demonstrated much higher rates of liberation than the PVC single layer films. The use of citric acid in the poly (vinyl alcohol) gave greater rates of release than with succinic acid.

Table 7 provides results of three-layer poly (vinyl alcohol) at 15°C. Film including citric acid showed very high rates of liberation for 22.9 days. Film including succinic acid showed a steadily increasing rate of liberation over the duration of the experiment (92.2 days).

It can be appreciated from the results presented in Tables 5-7 that films or materials according to the present invention may be tailored to provide a sulphur dioxide liberation rate suitable for different produce having widely varying requirements. For example, for grapes and freshly cut potatoes, the liberation rate may be ca. 30 mg of sulphur dioxide per kilogram of produce per day. Some grapes such as the thick skinned Ohanez may require a lower rate whereas thinner skinned Thompson seedless would require a higher rate of liberation. For wines the liberation rate may be about

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2mg per litre per day.

#### TOXICITY AND APPLICATIONS

The use of sulphur dioxide is generally regarded as being without any toxicity hazard at the usual levels but it does pose an important nutritional problem. The bisulphite (hydrogen sulphite) ion reacts readily and destructively, with the vitamin thiamine. Vegetables such as potatoes which are often stored in sulphite solutions at intermediate stages of processing will lose considerable proportions of their thiamine content. A further investigation by the user would be to determine that the foodstuffs packaged by this material are not the major source of thiamine.

A further drawback to the use of sulphite/SO<sub>2</sub> is taste. Above 500 ppm most people are aware of its disagreeable flavour and some can detect it at much lower levels. Some white wines are actually characterised by their slight sulphur dioxide flavour.

Sensitive asthmatics can suffer adverse reactions to sulphites/sulphur dioxide.

Other applications of the invention include:

- cut potato storage to prevent browning
- shrimp storage to prevent shrimp melanosis "black spot"
- Geofilms
- Lamination of structures in marine/aquatic environment
- Antifouling of marine/freshwater aquaculture nets
- Agricultural films e.g. mulch films
- Wine casks to prevent secondary fermentation and oxidation
- Dried fruit to prevent discoloration.

#### SHRIMP MELANOSIS

Shrimp melanosis, commonly termed "black spot", is a surface discoloration caused by enzymatic formation of

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precursor compounds which can polymerize spontaneously and/or react with cellular constituents to form insoluble pigments. This results in a cosmetic problem analogous to browning of potatoes, apples, avocados and grape juice resulting in reduced commercial value and consumer acceptance of the products. The endogenous shrimp enzyme, polyphenol oxidase (PPO) which catalyzes the initial step in black spot formation, remains active throughout post-harvest processing unless the shrimp are frozen or cooked. The PPO activity can resume in raw shrimp upon thawing. Likewise, the detrimental black pigments persist through processing and preparation unless bleached or marked.

Sulphiting agents were introduced in the 1950's to inhibit blackspot formation. Treatment of shrimp is by dipping them into a 1/25% sodium metabisulphite solution with an allowable sulphite residual of 10 ppm. Currently, this dip procedure is employed on commercial vessels followed by storage on crushed ice or brine freezing of the sulphited shrimp for subsequent transport and handling.

The present invention has significant impact for storage of the shrimp after the initial dipping described.

#### 25        GRAPES

Extended storage of grapes demands the control of decay arising from the infection by Botrytis cinerea spp. Sulfur dioxide is currently the only acceptable chemical to control decay. The chemical is applied to the grapes in commercial practice through a dual release system. The release system consists of kraft paper impregnated with sodium disulphite and a series of sachets containing about 0.3g of sodium disulphite. The migration of water activates the release of sulfur dioxide rapidly from the Kraft paper and more slowly

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from the sachets. These release systems are extremely sensitive to condensation and temperature abuse. If the temperature of the grapes is allowed to rise significantly above 5°C then the pads release the sulphur dioxide rapidly resulting in severe bleaching of the crop and short storage life because there is no sulfur dioxide available in the sachet.

This difficulty is avoided with the present invention where the liberation of sulphur dioxide is tempered by gentle acidification of the sulphur dioxide-liberating compound(s). The rate of liberation can be controlled by using different additives.

#### DRIED FRUIT

It has been found that dried apples when stored with sulphur dioxide-liberating materials retain their white appearance better than dried apples stored without sulphur dioxide-liberating materials. Accordingly, it is anticipated that the present invention shall also find application in the preservation of dried fruits.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

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Table 1Cellulose Acetate (CA) Films

Code	CA gram	Acetone ml	Glycerol gram	Na2S2O5 gram	CaSO3 gram	Tartaric gram	Citric gram
CANaTA	20	200	2.4	13	-	13	-
CANaCI	15	150	1.8	7.5	-	-	7.5
CACaTA	10	100	1.2	-	5	6.25	-
CACaCI	10	100	1.2	-	5	-	5.33

Table 2PVC Films

Code	Corvic gram	THF ml	Na2S2O5 gram	CaSO3 gram	Tartaric gram	Citric gram	Ascorbic gram	Lauric gram
VCCaTA	10	100	-	5	6.25	-	-	-
VCCaCI	10	100	-	5	-	5.33	-	-
VCNaAS	15	150	3	-	-	-	6	-
VCNaLAU	15	150	3	-	-	-	-	6.5



Table 3  
Poly (Vinyl Alcohol) Films

Code	PVOH gram	Water ml	Na2S2O3 gram	CaSO3 gram	Benzoic gram	Lactone gram	Ascorbic gram	Citric gram	Mon Suc acid gram
VHCa	15	110	-	7.5	-	-	-	-	-
VHBE	15	110	-	-	5.00	-	-	-	-
VHLA	15	110	-	-	-	3.30	-	-	-
VHAS	15	110	-	-	-	-	4	-	-
VHCa	30	220	-	12	-	-	-	-	-
VHCI	30	220	-	-	-	-	-	14	-
VHSU	30	220	-	-	-	-	-	-	11.8
VHNa	30	220	9.50	-	-	-	-	-	-
VHMX	30	220	-	-	-	-	-	7	5.9

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### Three-layer configuration

Code	Configuration
VHCaBE3:	Laminated VHCa-VHBE-VHCa
VHCaLA3	Laminated VHCa-VHLA-VHCa
VHCaAS3	Laminated VHCa-VHAS-VHCa
VHCaSU3:	Laminated VHCa-VHSU-VHCa
VHCaSU2	Laminated VHCa-VHSU
VHCaCI2	Laminated VHCa-VHCI
VHVCNaCI3	Laminated VHNa-VHCI-PVC
VHCaCI3	Laminated VHCa-VHCI-VHCa
VHCaSU3	Laminated VHCa-VHSU-VHCa

Table 4Poly (Vinyl Alcohol) (PVOH) film with copper or iron salt as oxidant

Code gram	PVOH gram	Water gram	Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> gram	CuSO <sub>4</sub> gram	FeSO <sub>4</sub> gram	Cat.Content ppm
VHNa25CU1500	30	200	7.5	0.0455	0	1517
VHNa25CU500	30	200	7.5	0.0169	0	563
VHNa25FE1500	30	200	7.5	0	0.0598	1993
VHNa25FE500	30	200	7.5	0	0.015	500
VHNa25O000	15	100	3.75	0	0	0
VHNa25CU100	30	200	7.5	0.0045		150

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Table 5  
Results of release of sulfur dioxide ug/m2 from films

TIME(days)	VCCaCI	CANaCI	VHCaAS3	TIME (days)	VHCaBE3	VHCaIA3	Kraft Paper	UVAS Sachet
0.0	0	0	0	0.0	0	0	0	2
1.0	3	101	0	0.8	3	277	11	13
3.2	13	1122	0	5.0	19	471	11	23
4.0	13	5523	0	7.9	22	1263	39	71
8.2	1104	1987	27	13.7	30	1434	49	114
11.1	1753	2197	31	14.7	38	1966	112	144
16.9	2242	2261	36	18.0	42	2617	273	219
18.0	2271	2270	42	20.9	65	3145	409	298
21.2	2354	2274	59	26.9	74	3384	NFR	NFR
24.1	2477	2296	61	32.0	NFR	3411		
30.1	2567	2307	NFR	32.7		3411		
35.2				32.7		3424		
				34.0		3475		
				35.7		3536		
				36.0		3623		
				38.7		3642		
				40.7		3678		
				41.7		3697		
				45.7		3762		
				47.8		3770		
				48.7		3793		
				52.9		3819		
				54.7		3859		
				56.7		3906		
				59.7		3910		
				61.7		3933		
				66.7		3982		
				67.7		3987		
				69.7		3998		
				70.7		4022		
				75.7		4045		
				77.7		4068		
				80.7		4072		

NRF = No further Release

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Table 6

Amount (ug/m<sup>2</sup>) Sulfur dioxide released at 0°C

TIME (days)	VcNaMX	VCCaCI	VcNaSU	VHCaSU2	VHCaCI2
0.0	0	0	0	0	0
0.9	8	7	3	2	3
1.9	13	12	4	6	31
4.8	25	19	8	128	246
5.7	29	21	10	172	364
6.8	31	24	11	263	522
7.7	33	26	11	321	668
8.8	35	28	12	353	863
11.7	41	33	14	382	1329
12.8	43	35	14	389	1469
14.8	45	36	15	396	1610
15.7	45	37	15	405	1717
18.8	50	40	17	437	2042
19.7	51	41	17	440	2130
20.7	52	42	18	457	2225
21.7	53	43	18	461	2320
22.7	54	45	18	462	2415
25.7	56	48	19	466	2807
26.7	57	49	19	489	2884
27.7	58	50	20	497	2974
29.0	59	50	20	506	3089
29.7	60	51	20	510	3156
32.7	63	54	21	532	3444
33.7	64	54	22	538	3487
34.7	65	55	22	547	3545
35.7	65	56	22	549	3572
36.7	67	57	24	553	3618
39.7	68	59	25	568	3678
41.0	69	59	25	584	3720
41.8	70	60	25	590	3755
42.8	70	60	25	592	3765
43.7	72	61	26	597	3884
46.7	76	63	26	604	3818
47.7	77	64	27	615	3829
48.7	78	64	27	623	3837
49.7	79	65	27	629	3846
50.7	80	65	28	633	3854
53.7	81	66	28	636	3869
54.7	82	67	28	651	3879
55.7	82	67	28	656	3887
56.7	84	67	NFR	658	3893
57.7	85	68		662	3897
60.7	86	69		671	3915
61.7	87	69		683	3916
65.0	94	72		758	3924
68.7	96	73		860	3925
70.7	96	74		890	3226
75.7	97	75		978	3938
77.9				1001	3945
81.7				1011	3958
85.7				1018	3966
97.7				1031	3987
102.7				1038	3996

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Table 7Amount (ug/m<sup>2</sup>) Sulfur dioxide released at 15°C

Days	VHCaCI3 ug/m <sup>2</sup> film	VHCaSU3 ug/m <sup>2</sup> film
0.0	0.0	0.0
0.2	16.1	6.1
1.0	623.8	85.1
1.3	771.7	102.3
1.9	1361.1	137.8
4.9	4540.6	276.6
5.9	5280.8	324.9
6.9	5734.2	375.5
8.0	6648.4	463.8
11.9	7198.2	567.7
13.0	7237.2	607.1
14.9	7288.0	654.5
15.9	7294.3	674.0
19.0	7335.5	805.6
19.9	7339.2	823.3
20.9	7347.1	864.4
22.0	7353.4	890.0
22.9	7356.0	931.6
26.0	NFR	1082.4
28.9		1175.4
35.0		1239.7
39.9		1297.7
47.1		1583.4
54.1		1963.0
58.2		2104.8
65.0		2167.0
72.0		2415.9
79.1		2704.2
86.2		2818.6
92.2		3026.8

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CLAIMS:-

1. A polymeric film material for use in packaging of produce, incorporating a sulphur dioxide-liberating compound(s) and one or more of the following additives:
  - 5 - an acid compound(s);
  - a hygroscopic compound(s);
  - a polymer(s) which degrades to produce an acid;
  - a compound(s) which becomes or generates an acid or acidic gas in a humid environment;
- 10 wherein the amount and identity(ies) of the additive(s) are selected to provide a predetermined, controlled rate of sulphur dioxide liberation.
2. A polymeric film material according to claim 1, wherein the sulphur dioxide-liberating compound(s) is  
15 selected from the group consisting of sodium sulphite, sodium hydrogen sulphite, sodium metabisulphite, calcium sulphite, calcium hydrogen sulphite calcium metabisulphite, salts of thiosulphuric acid, organic sulphur dioxide-liberating agents and mixtures thereof.
- 20 3. A polymeric film material according to claim 1 or 2, wherein the one or more additives comprises an acid compound(s) selected from the group consisting of stearic acid, benzoic acid, citric acid, ascorbic acid, succinic acid, tartaric acid, sorbic acid, acetic acid, propionic  
25 acid, adipic acid, fumaric acid, lactic acid, malic acid, phosphoric acid and their salts.
4. A polymeric film material according to claim 1 or 2, wherein the one or more additives comprises citric acid.
5. A polymeric film material according to claim 1 or 2,  
30 wherein the one or more additives comprises a mixture of acid compounds one of which is stearic acid.
6. A polymeric film material according to any one of the preceding claims, wherein the one or more additives comprises a hygroscopic compound(s) selected from the  
35 group comprising salts of acetic acid, salts of

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hydrochloric acid, salts of carbonic acid, glycerol and propylene glycol.

7. A polymeric film material according to any one of the preceding claims, wherein the one or more additives  
5 comprises a polymer(s) which degrades to produce an acid selected from the group consisting of neoprene, poly(lactic acid), poly(glycolic acid) and co-polymers, poly(anhydrides) and poly(ortho-esters).

8. A polymeric film material according to any one of the  
10 preceding claims, wherein the one or more additives comprises a compound(s) which becomes acid in a humid environment selected from the group consisting of anhydrides, lactones and lactides.

9. A polymeric film material according to any one of the  
15 preceding claims, wherein the film material comprises polymers selected from the group consisting of polyolefins, poly(vinyl chloride), ethylene-vinyl alcohol, acid functional polymers, cellulose acetate, ethyl cellulose, starch, ionomers and poly (vinyl alcohol).

20 10. A polymeric film material according to claim 9, wherein the film material comprises poly (vinyl alcohol).

11. A polymeric film material according to any one of the preceding claims, wherein the film material comprises multiple layers of polymeric film.

25 12. A polymeric film material according to claim 11, wherein the sulphur dioxide-liberating compound(s) and the one or more additives are present in different film layers.

13. A material for use in packaging of produce,  
comprising at least two laminated layers, wherein at least  
30 one layer incorporates a sulphur dioxide-liberating compound(s) and at least one other layer incorporates one or more of the following additives:

- an acid compound(s);
- a hygroscopic compound(s);
- 35 - a polymer(s) which degrades to produce an acid;

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- a compound(s) which becomes or generates an acid or acidic gas in a humid environment;  
the arrangement and characteristics of the layers being such that the additive(s) cause or influence the
- 5 liberation of sulphur dioxide.
14. A material according to claim 13, wherein the sulphur dioxide-liberating compound(s) is selected from the group consisting of sodium sulphite, sodium hydrogen sulphite, sodium metabisulphite, calcium sulphite, calcium hydrogen
- 10 sulphite, calcium metabisulphite, salts of thiosulphuric acid, organic sulphur dioxide-liberating agents, and mixtures thereof.
15. A material according to claim 13 or 14, wherein the one or more additives comprises an acid compound(s)
- 15 selected from the group consisting of stearic acid, benzoic acid, citric acid, ascorbic acid, succinic acid, tartaric acid, sorbic acid, acetic acid, propionic acid, adipic acid, fumaric acid, lactic acid, malic acid, phosphoric acid and their salts.
- 20 16. A material according to claim 13 or 14, wherein the one or more additives comprises citric acid.
17. A material according to claim 13 or 14, wherein the one or more additives comprises a mixture of acid compounds one of which is stearic acid.
- 25 18. A claim according to any one of claims 13 to 17, wherein the one or more additives comprises a hygroscopic compound(s) selected from a group consisting of salts of acetic acid, salts of hydrochloric acid, salts of carbonic acid, glycerol and propylene glycol.
- 30 19. A claim according to any one of claims 13 to 18, wherein the one or more additives comprises a polymer(s) which degrades to produce an acid selected from the group consisting of neoprene, poly(lactic acid), poly(glycolic acid) and copolymers, poly(anhydrides) and
- 35 poly(ortho-esters).



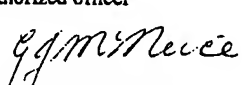
- 23 -

20. A material according to any one of claims 13 to 19, wherein the one or more additives comprises a compound(s) which becomes acid in a humid environment selected from the group consisting of anhydrides, lactones and lactides.
- 5 21. A material according to any one of claims 13 to 20, which comprises at least two laminated polymeric film layers.
22. A material according to claim 21, wherein the at least two laminated film layers comprise polymers selected  
10 from the group consisting of polyolefins, poly (vinyl chloride), ethylene-vinyl alcohol, acid functional polymers, cellulose acetate, ethyl cellulose, starch, ionomers and poly (vinyl alcohol).
23. A material according to claim 21 wherein the at least  
15 two polymeric film layers comprise poly (vinyl alcohol).
24. A claim according to any of claims 13 to 23, wherein the amount and identity(ies) of the additive(s) are selected to provide a predetermined, controlled rate of sulphur dioxide liberation.
- 20 25. A method for producing a polymeric film material according to claim 12, comprising separately forming at least one film layer incorporating the sulphur dioxide-liberating compound(s) and at least one film layer incorporating the one or more additives, and thereafter  
25 laminating the film layers together.
26. A method for producing a material according to any one of claims 21 to 24, comprising separately forming at least one layer incorporating the sulphur dioxide liberating compound(s) and at least one layer  
30 incorporating the one or more additives, and thereafter laminating the film layers together.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 93/00562

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int. Cl. <sup>5</sup> C08K 3/00 3/30 5/00 5/41 5/42 13/02 C08L 57/00 1/12 27/06 29/04 B32B 27/18 A23 L 3/3445 A23B 7/152 4/16 B65D 65/38 81/28  According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b>  Minimum documentation searched (classification system followed by classification symbols) IPC C08K 3/00, 3/30, 5/00, 5/41, 5/42, 13/02, C08L, 57/00, 1/12, 27/06, 29/04, B32B 27/18, A23L 3/3445, A23B 7/152, 4/16, B65D 65/38, 81/28  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU:IPC C08K 3/00, 3/30, 5/41, 5/42, 13/02, C08L 27/06  Electronic data base consulted during the international search (name of data base, and where practicable, search terms used) DERWENT IPC as above Packag: and Sulph: and Sulf: and dioxid: and film # and wrap.				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.		
A	AU,B, 24472/77 (514221) (M.A. THORP) 26 October 1978 (26.10.78) page 2 lines 16-26	1-26		
A	AU,A, 22303/83 (BENSON AND BROWN) 21 June 1984 (21.06.84) page 4 lines 8-26	1-26		
A	FR-A-2536045 (CROSS) 20 May 1984 (20.05.84) page 2 lines 20-36	1-26		
<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="display: flex; align-items: center;"> <input type="checkbox"/> Further documents are listed in the continuation of Box C.         </div> <div style="display: flex; align-items: center;"> <input checked="" type="checkbox"/> See patent family annex.         </div> </div>				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="width: 50%; vertical-align: top;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </td> </tr> </table>			<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>
<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>			
Date of the actual completion of the international search 3 February 1994 (03.02.94)		Date of mailing of the international search report 14 FEB 1994 (14.02.94)		
Name and mailing address of the ISA/AU  AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA  Facsimile No. 06 2853929		Authorized officer   GRANT McNEICE  Telephone No. (06) 2832055		

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
AU	24472/77	AT	3030/77	AT	354877	BE	853813
AU	514221	CA	1097333	CY	1100	DE	2718742
		DK	1861/77	DK	148626	FR	2349508
		GB	1572902	IE	45138	IT	1076727
		IT	1076727	LU	77177	NL	7704756
		PT	66482	US	4188457	ZA	7702223
AU	22303/83	ES	528040	ES	8504440	ES	290963
		FR	2555552	GR	79708	IL	70343
		IT	8349500	IT	1197757	PT	77819
		ZA	8301865				
FR	2536045	GR	77825	IT	8224771	IT	1205287
		ES	8400961	ES	517389		
END OF ANNEX							